Photopolymers exhibiting a large difference between glass transition and curing temperatures

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When the glass transition temperature T_g of a completely polymerized system is considerably higher than the temperature of polymerization, the reaction usually stops before completion. With step reactions the difference between T_g and T_{cure} rarely exceeds 35 K. We have found that in the chain crosslinking photopolymerization of 1,6-hexanediol diacrylate a difference of more than 70 K can be observed. Photopolymerization continues in the glassy state, albeit at a self-decelerating rate. Possible causes of this continuation are (i) the presence of a significant amount of unreacted monomer up to high conversions and (ii) the persistence of a localized mobility of radical sites in the glassy state through tertiary hydrogen abstraction. It is proposed that the continuation of the reaction is not limited by vitrification but by freezing of secondary relaxations. The initial, fast part of the photopolymerization process was monitored with differential scanning calorimetry (d.s.c.), the slow continuation in the glassy state with Fourier-transform infra-red spectroscopy (*FT*i.r.). By using thin silicon substrates the same samples could be used with both techniques. In the range of conversions accessible with d.s.c., a perfect correlation with *FT*i.r. results was obtained. This proves that Beer's law applies to the i.r. data.

(Keywords: vitrification; chain crosslinking; polymerization; networks; glass transition; photopolymerization; diacrylate)

INTRODUCTION

The room-temperature photopolymerization of multifunctional acrylates usually leads to glassy polymers in which only a part of the available double bonds are reacted[1]. Before completion of conversion the vitrification process decelerates the reaction to a hardly perceptible rate. Only very flexible oligomers in which the reactive groups are relatively far apart can be completely reacted at ambient temperature, an example being certain siloxane or urethane acrylates[2].

Vitrification before completion of the reaction is also observed with many thermally cured epoxides[3–6] when the curing temperature T_{cure} is significantly below the glass transition temperature T_g of the completely cured network. It is generally accepted that the glass transition temperature will not exceed the curing temperature by more than 50 K, an empirical limit being 25–35 K[4] or 15–30 K[5,6].

Contrary to epoxides, cured in a thermally activated step reaction, relatively little work has been done on the vitrification occurring during chain crosslinking photopolymerization. Besides the technological interest in making polymers with a high T_g at ambient temperature, there is also a mechanistic argument for studying the continuation of photopolymerization in the glassy state. In chain crosslinking systems beyond gelation the sol fraction consists of pure monomer whereas in step reactions it consists of a mixture of oligomers. This difference might in principle show up as a difference in rate in the end-phase of the reaction since small molecules generally maintain a certain mobility, even in glassy polymers, whereas oligomers are probably more restricted in their mobility.

Therefore we have investigated the continuation of photopolymerization in the glassy state as well as the relation between curing temperature and glass transition temperature of photopolymerized 1,6-hexanediol diacrylate (HDDA).

Previous work in this area has been carried out with epoxy acrylates[7–9] and urethane acrylates[10]. However, since intense light sources were used in these investigations the temperature rise of the samples caused by the heat of reaction and the infra-red emission of the light source could not be controlled. This probably explains the observation of T_g values of up to 130°C for epoxy acrylates that were cured by irradiation at room temperature[8]. In this respect it is relevant to refer to our previous observation that at an intensity of only 1.5 mW cm^{-2} temperature rises of more than 100°C are easily obtained in samples of 1 mm thickness[11]. A further point of concern is that heating of the sample during measurement of T_g may induce additional, unwanted polymerization, especially since glassy photopolymers may contain a considerable amount of trapped radicals[1,12].

In order to check for sample changes during thermal treatment we ran two parallel series of experiments, one for measuring T_g in a dynamic mechanical thermal analysis (d.m.t.a.) apparatus and another for measuring the extent of reaction and changes in it. The latter series was photopolymerized in the d.s.c., using thin silicon substrates instead of d.s.c. pans, such that subsequent changes could be monitored using transmission *FT*i.r. spectroscopy. The coupling of d.s.c. with *FT*i.r. also enabled us to check the validity of Beer's law in the *FT*i.r. measurement of conversion, thereby increasing the reliability of the results.

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By combining d.s.c., *FT*i.r. and d.m.t.a. we were able to investigate the polymerization process before and during the vitrification process and to monitor the accompanying changes in $T_{\tan\delta,\max}$.

EXPERIMENTAL

Chemicals

1,6-Hexanediol diacrylate (HDDA) (Röhm, Darmstadt, FRG) was purified by repeated recrystallization, followed by solvent-free chromatography over basic alumina in order to remove the inhibitor. Thiol addition analysis showed a C=C double bond concentration of 97.3% of the theoretical amount.

The photoinitiator α,α-dimethoxy-α-phenylacetophenone (DMPA) was supplied by Ciba Geigy (Basel, Switzerland) and used as received.

All experiments were performed with a 0.25 wt% solution of DMPA in HDDA.

Sample preparation

Quantitative (*FT*) infra-red absorbance measurements of bulk polymers, using strong absorption bands, are restricted to rather thin layers (1–10 μm). In the case of poly(HDDA) free films of this thickness cannot be handled because of their extreme brittleness. Therefore samples were measured as a coating on an infra-red-transparent substrate. For this purpose we used single-crystalline silicon wafers of 7 mm diameter and a thickness of 0.25 mm. These wafers were polished on both sides in order to avoid transmission losses due to scattering. After degreasing the wafers ultrasonically in 2-propanol for 15 min, 0.2 μl of the sample was applied and spread evenly by slowly rotating the disc and simultaneously moving the tip of the syringe from the centre to the edge of the wafer. In this way we obtained a circular layer approximately 6 mm in diameter and with an average thickness of 7 μm. A small area was left uncoated to prevent wetting of the rim. Next the sample was placed in the d.s.c. and allowed to equilibrate with the nitrogen purge gas for 15 min; then it was irradiated with u.v. light for a selected time. After exposure and decay of the rate the sample was mounted in a holder and transferred to the *FT*i.r. spectrometer.

Bulk d.m.t.a. samples were prepared by irradiation of the solution in a metallic mould. For this purpose we used an aluminium block with a machined recess with dimensions of 40 mm length × 10 mm width × 0.5 mm depth. After cleaning the mould, using 2-propanol, it was filled up to the edge with the liquid and subsequently placed in a vessel provided with a quartz glass window. Before irradiation the vessel was purged with pure nitrogen ($[O_2] < 2$ ppm) for 4 h in order to assure quantitative removal of dissolved oxygen. U.v. exposure was carried out using a Philips TL 08/4W fluorescent lamp ($\lambda_{max} = 350$ nm). The light intensity was varied by means of neutral density filters and it was measured with an International Light 745A UV Curing Radiometer. After irradiation the samples were kept overnight in air to allow for decay of trapped radicals.

Samples for thermogravimetric analysis were prepared in the same way as those used for d.m.t.a., only the size was reduced to approximately 5 mm × 5 mm × 0.5 mm.

Calorimetry

Isothermal d.s.c. measurements were performed on a Perkin Elmer DSC-2C, modified for u.v. irradiation[13,14]. Instead of conventional sample pans, thin silicon wafers with a sample layer of approximately 7 μm thickness were used. Before and during exposure the sample chamber was flushed with pure nitrogen ($[O_2] < 2$ ppm). The same u.v. source and control of light intensity was used as in the case of d.m.t.a. sample preparation. Polymerization reactions were carried out at a temperature of 20°C.

Infra-red spectroscopy

*FT*i.r. spectra were recorded on a Bruker IFS 45 spectrometer. On mounting the sample its edge was covered, so only radiation from the centre part (5 mm diameter) was allowed to reach the detector. In this way inaccuracies due to layer thickness variations across the i.r. beam were minimized. Some 400 scans were collected with a relatively low resolution of 8 cm^{-1}, which was chosen in order to eliminate interference fringes.

Dynamic mechanical thermal analysis

D.m.t.a. measurements were made with a Polymer Laboratories instrument. Samples were clamped in the single cantilever mode with 2 mm distance between the clamps. Spectra were recorded at a frequency of 1 Hz and a strain amplitude of 16 μm. Temperature scans were carried out in air at a heating rate of 4 K min^{-1}.

Thermogravimetric analysis

A Perkin Elmer TGS-2 was used for recording weight losses of polymer samples upon heating in nitrogen at a rate of 5 K min^{-1}.

Conversion measurements

In general, quantitative infra-red spectroscopy suffers from a non-linear relationship between absorbance and concentration owing to instrumental inadequacies (stray light, poor resolution compared to absorption bandwidths), sample preparation (non-uniform layer thickness, surface irregularities) and because of sample-specific phenomena (association or dissociation). Moreover, if concentration changes are accompanied by changes in state of aggregation, then deviations from Beer's law may be quite large. Upon polymerization of HDDA, the density increases by approximately 15%, and the viscosity changes over many orders of magnitude. Therefore, quantitative measurements of conversion should be established using an empirical relationship between absorbance and concentration. This was done by polymerizing samples in the d.s.c. to a known extent, after which the samples were used for infra-red absorption measurements. The decrease of the C=C double bond was evaluated using the absorption band at 810 cm^{-1}, γ_t(CH). The difficulty in obtaining accurate values for the thickness of these thin samples requires the use of an internal standard.

The absorbance at 810 cm^{-1} was measured relative to the absorbance of a reference band. For this purpose the $\nu_s(CH_2)$ vibration at 2862 cm^{-1} was chosen since in HDDA:

(i) the baseline of this isolated band can be determined accurately;

(ii) the intensity of the absorption is comparable to the absorbance of the 810 cm^{-1} band of the monomer;

(iii) the peak width and position do not change upon polymerization.

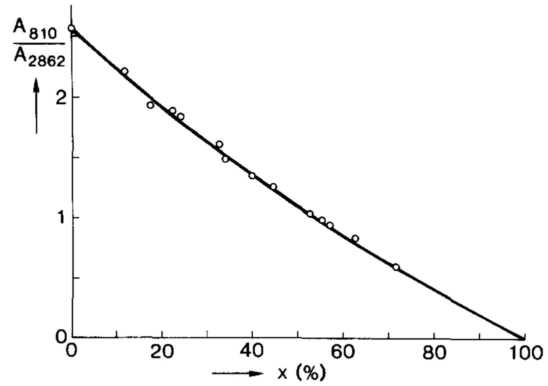

Figure 1 Ratio of i.r. absorbances of HDDA at 810 cm^{-1} and 2862 cm^{-1} vs. extent of double-bond conversion x, measured with d.s.c.: (○) measured values; (——) calculated, using the absorbance ratio at $x=0$. Intensity, 0.2 mW cm^{-2}; initiator, 0.25 wt% DMPA; temperature, 20°C

A disadvantage of the use of this particular reference band may be that its intensity increases with conversion of $=CH_2$ to $-CH_2-$. However, this effect can be easily corrected for mathematically.

In *Figure 1* the calculated absorbance ratio is plotted as a function of the extent of conversion. The calculation is based on the experimental value of $A(810\,cm^{-1})/A(2862\,cm^{-1})$ for monomeric HDDA (conversion $x=0$), assuming the validity of Beer's law. In the same figure measured absorbance ratios of partly polymerized samples are plotted against their extent of conversion as measured with d.s.c. All experimental values, ranging from 12 to 70% conversion, agree very well with the theoretical relationship (full curve), and therefore the latter was assumed to apply over the entire range up to 100% conversion.

However, at larger conversions, as observed during vitrification of the sample, the correlation between d.s.c. and i.r. results broke down.

Effect of thickness on sample conversion

There may be a slight difference between the d.s.c. and d.m.t.a. samples that were exposed at 2 mW cm^{-2} since the somewhat thicker d.m.t.a. sample will have been heated by several tens of degrees kelvin by the liberation of the heat of polymerization[11]. However, it is rather unlikely that this will have caused excessive conversion since the maximum heat flux is produced at the rate maximum which occurs at 30% conversion[1,15]. Beyond the maximum the temperature drops rapidly. At 2 and 0.2 mW cm^{-2} the maximum is reached after 5.5 and 10.5 s, respectively, whereas the 'tail' of the reaction extends over several minutes. Moreover, the effect of heating on the rate of propagation is counteracted by a diminution of the Trommsdorff effect.

RESULTS AND DISCUSSION

Influence of intensity and dose on conversion

Table 1 shows the extent of double-bond conversion of a series of samples, measured with d.s.c. as well as with *FT*i.r., at four different light intensities, covering a range of three decades. The exposure times were determined by the sensitivity of the d.s.c.: irradiation was interrupted at the moment the rate fell below the limit of detection. The samples were then exposed to air.

The nice correlation between d.s.c. and i.r., shown in *Figure 1*, obviously breaks down at very low rates and during vitrification. Extends of conversion obtained with *FT*i.r. are significantly larger than those obtained with d.s.c., notably at low light intensities. Presumably the polymerization reaction has continued in the glassy state although unobserved with d.s.c. The latter method, in which rate rather than conversion is monitored, is less suited for conversion measurements of very slow processes.

The polymers were further characterized by measurement of the temperature of maximum mechanical loss at 1 Hz rather than by recording the jump in specific heat with d.s.c. This choice was imposed by the lack of sensitivity of the d.s.c. for detection of transitions in densely crosslinked polymers. Comparable experimental conditions were used to prepare samples for dynamic mechanical thermal analysis. Temperatures of maximum mechanical loss at 1 Hz, $T_{\tan\delta,\max}$, are given in *Table 1* and mechanical loss curves are shown in *Figure 2*. The d.m.t.a. measurements reveal a large increase of $T_{\tan\delta,\max}$ with light intensity, probably due to the increase in the extent of double-bond conversion x.

The increase of 'final' conversion with intensity has been attributed to delayed shrinkage with respect to conversion[1,14], thus maintaining a high mobility of unreacted vinyl groups for some time. With a high intensity a large fraction of the vinyl groups will react in the unrelaxed state; at a low intensity more vinyl groups will remain unreacted till relaxation has occurred. Then, however, their propensity to react will also have declined due to lack of mobility.

Table 1 Extent of double-bond conversion of HDDA, determined with d.s.c. and with *FT*i.r., and temperature of maximum mechanical loss of samples polymerized at different light intensities. Exposure continued as long as heat flux could be detected with d.s.c. Temperature: 20°C. Initiator: 0.25 wt% DMPA

Light intensity (mW cm^{-2})	Exposure time (min)	x(d.s.c.) (%)	x(*FT*i.r.) (%)	$T_{\tan\delta,\max}$ (°C)
0.002	25	44.5[a]	61.5	−23
0.02	15	57.5	68	12
0.2	12	72	75	43
2	7.5	81	79.5	62

[a] Inaccurate value

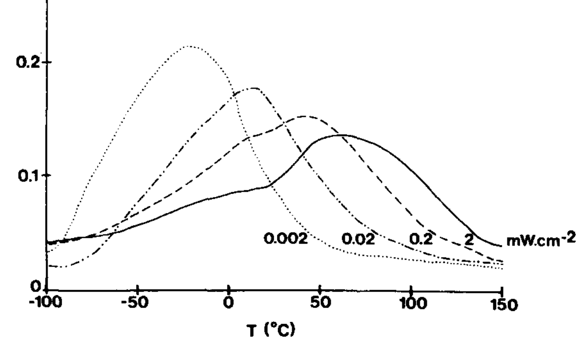

Figure 2 Mechanical loss tangent of HDDA samples, polymerized at different light intensities, vs. temperature. Exposure times, see *Table 1*; temperature of polymerization, 20°C; initiator, 0.25 wt% DMPA

So there are in principle two regimes of the polymerization rate, a fast reaction in the unrelaxed state followed by a much slower process in the almost completely relaxed vitreous state. However, it is difficult to define the transition between the two.

The slow process had remained unobserved when we interpreted the apparent dependence of 'final conversion' on light intensity[1,14]. With the present view the times after which the irradiations of the d.m.t.a. samples were stopped appear to be rather arbitrarily chosen but we then did not expect a significant increase of the conversion in the glassy state.

In a second series of samples the exposure times at all but the highest intensity were extended in order to obtain equal doses. Results are listed in *Table 2*, and mechanical loss curves are shown in *Figure 3*. Obviously, d.s.c. conversion measurements did not yield higher values when the irradiation time was increased, but *FT*i.r. analysis as well as d.m.t.a. showed that polymerization had proceeded significantly, albeit at a very low rate.

We also checked for a possible dark reaction by irradiating a sample for 25 min at the lowest intensity and keeping it under nitrogen till 7500 min had passed. In this case we measured a $T_{\tan\delta,\max}$ of 6°C, so some reaction indeed occurred in the dark. However, the rise of $T_{\tan\delta,\max}$ upon irradiation is considerably larger, so light-induced reaction must have occurred in the glassy state.

So, on applying equal doses, we have obtained materials with rather similar properties. This was not anticipated on account of our previous d.s.c. results[14]. In fact, chemical conversion appears to be even higher at the lower intensities where any undesired heating can be excluded. This can be explained as follows.

In ideal, unperturbed systems the rate of light-induced chain polymerizations is proportional to the square root of the light intensity. The kinetic chain length, however, varies with the inverse square root of the light intensity[16]. Therefore, when equal doses are applied using different intensities the highest extent of double-bond conversion is expected at the lowest light intensity. If termination took place by a first-order process, no intensity dependence would be anticipated.

Table 2 Same as *Table 1*, but exposure times adapted to obtain equal irradiation doses

Light intensity (mW cm^{-2})	Exposure time (min)	x(d.s.c.) (%)	x(*FT*i.r.) (%)	$T_{\tan\delta,\max}$ (°C)
0.002	7500	44.5^a	85	85
0.02	750	58	85.5	87
0.2	75	70.5	80	73
2	7.5	81	79.5	62

^{a} Not measured separately but value taken from *Table 1*

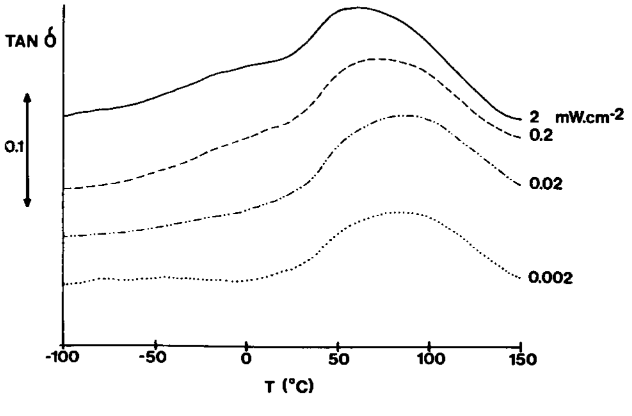

Figure 3 Loss curves as in *Figure 2*, but with exposure times adapted to obtain equal irradiation doses (see *Table 2*)

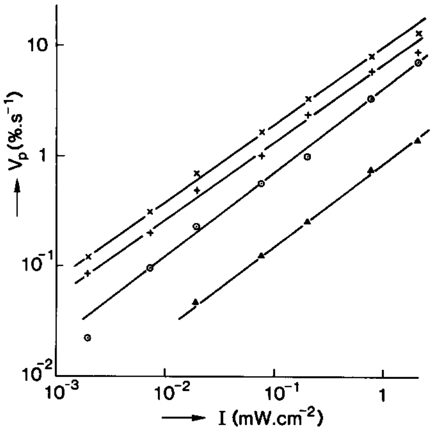

Figure 4 Rate of polymerization of HDDA vs. light intensity. Rates were determined at 20°C for $x=0.1$ (+), $x=0.3$ (×), $x=0.5$ (○), $x=0.6$ (▲). Initiator, 0.25 wt% DMPA

Owing to autoacceleration and trapping of radicals (combined first- and second-order termination) the bulk polymerization of HDDA behaves far from ideally. This manifests itself as a different intensity dependence of the rate of polymerization. The data in *Figure 4* show that the rate of polymerization increases with $I^{0.7}$ (ref. 17). Since the intensity exponent is found to be between 0.5 and 1.0, combined first- and second-order termination is likely to occur. Therefore, the highest conversion is still expected at the lowest intensity. This is in line with our observations.

Reaction in the vitreous state

The d.s.c. and *FT*i.r. results clearly illustrate the self-decelerating character of the chemical reaction. Upon polymerization the system passes through the glass transition isothermally. The mobility of the unreacted double bonds is thereby strongly reduced. In this way the rate decreases to a level that is far below 1% of the maximum rate, although 20% of the double bonds are still present. Nevertheless, even in the glassy state, diffusion of free monomer is still possible as well as transport of reactive sites via tertiary hydrogen abstraction[15]. Conversion will therefore continue to increase with time, as long as the irradiation is continued and initiator is present, until a topological limit is reached[6].

The continuation of the reaction can be demonstrated by further increasing the exposure dose. In order to limit the duration of the experiment, it was carried out at the highest available light intensity. *Table 3* shows that the double-bond conversion continues to increase with irradiation time, but at a steadily decreasing rate. Mechanical loss curves are shown in *Figure 5*. Thus, vitrification causes the propagation rate to become diffusion-limited.

From the results in *Table 3* it can be deduced that the same applies to the rate of initiation. Light-induced dissociation, followed by reaction of the initiator fragments with monomer or other species, lowers the concentration of photoiniator. In a dilute solution in

Table 3 Extent of double-bond conversion of HDDA, determined with d.s.c. and with *FT*i.r. and temperature of maximum mechanical loss of samples polymerized at different exposure times (cf. *Table 1*)

Light intensity ($mW\,cm^{-2}$)	Exposure time (min)	x(d.s.c.) (%)	x(*FT*i.r.) (%)	$T_{\tan\delta,\max}$ (°C)
2	7.5	81	79.5	62
2	75	82.5	85	82
2	750	82	89.5	87
2	7500	82[a]	92	93

[a] Not measured separately but average value of conversions measured at shorter exposure times

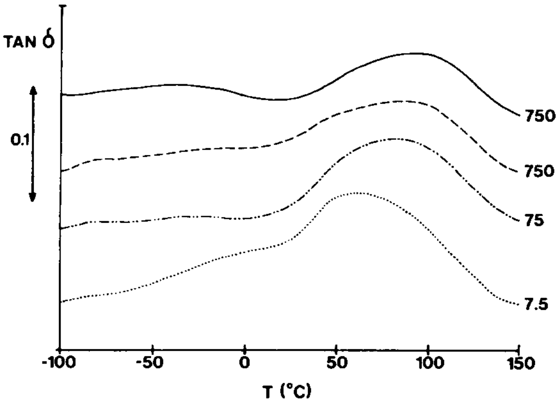

Figure 5 Mechanical loss tangent of HDDA samples, polymerized at $2\,mW\,cm^{-2}$, for various irradiation times. Initiator, 0.25 wt% DMPA; temperature of polymerization, 20°C

2-propanol exposed at $2\,mW\,cm^{-2}$, DMPA showed a neat first-order decay with a half-life of 2.5 min. If these kinetics were also valid in our polymerizing system, more than 10% of the initial amount would be left after 7.5 min, but the concentration would have been reduced to 10^{-9} times its initial value after 75 min. Yet polymerization has continued, so the rate of photolysis of DMPA appears to have slowed down considerably in the glassy environment. Apparently vitrification favours cage recombination of primary radicals and thereby reduces the efficiency of initiator decay and initiation.

Premature slowing down of the polymerization reaction is not only observed with diacrylates forming densely crosslinked networks, but also with some difunctional monomers, for instance in the low-temperature polymerization of methyl methacrylate[18,19]. Similar observations have been made with networks of amine-cured epoxides[3–6].

Glass transition temperature and curing temperature

In general, the difference between the glass transition temperature of isothermally vitrified materials and the temperature of reaction does not exceed 15–35°C[4–6]. However, d.m.t.a. measurements of poly(HDDA) show temperatures of maximum mechanical loss up to 93°C, which is more than 70° above the temperature of polymerization. This result seems at variance with the general observation. The latter is usually explained by noting that in the liquid state the rate is governed by an Arrhenius equation, i.e. by thermal activation, but that in the glassy state it is controlled by diffusion, i.e. by volume activation. The rate during isothermal vitrification can then be described by a WLF-type equation of the form:

$$\ln k = a(T - T_g)/(T - T_g + c)$$

where a and c are constants and T_g is the conversion-dependent glass transition temperature[4]. When T_g approaches the value of $T + c$, the rate goes to zero. If the analogy of the rate equation with the WLF equation were complete, c would be expected to be 50 K. However, it is well known that the applicability of the WLF equation ceases below T_g. In practice the value of c has been shown to be about 25–35 K.

Recently, Dušek has proposed another rate equation which is based on the Adam and Gibbs equation for the configuration entropy and on the assumption that this entropy goes to zero at $T_g - 50\,K$[20]. This implies again that the rate of polymerization also goes to zero at this temperature since the displacement of reactants necessarily requires some kind of rearrangement of the polymer matrix.

However, comparison with physical ageing of linear polymers shows that localized rearrangements may still occur between T_g and T_β. Below T_β physical ageing is almost completely arrested[21]. In a polymer with a high concentration of radicals ($\simeq 10^{-3}$ M), part of which are trapped and part of which can migrate through the network by successive abstraction of tertiary hydrogen atoms[15] and with a high concentration of unreacted double bonds, it is likely that each reaction step will require only a restricted local rearrangement. Moreover, each step also generates an additional amount of free volume. Therefore it seems probable that chemical reaction will proceed at least as long as physical ageing continues, unless a topological limit of conversion is reached[6]. The curves in *Figure 5* provide some evidence for the presence of secondary maxima of $\tan\delta$ at temperatures below 0°C. If these shallow maxima refer to real transitions, relaxation is likely to occur at ambient temperature.

Upon vitrification, chain reactions may behave somewhat differently from step reactions since in the former case a significant amount of unreacted monomer molecules is present up to high conversions. Small molecules will continue to diffuse when vitrification sets in; indeed quite often there is even no discontinuity in the diffusion coefficient[22,23]. In step reactions continuation of the reaction generally requires the movement of relatively large oligomers, the motion of which will be suppressed at a much earlier stage.

Nevertheless, recently Peng and Gillham observed large differences of up to 70 K between T_g and T_{cure} of amine-cured epoxides[24]. Unfortunately, no conversions were reported and no account was given of the possible contribution of degradation reactions. For samples kept at 190°C for 10 days, such processes cannot *a priori* be excluded. With the radical polymerization of HDDA a stage will eventually be reached where virtually all of the free monomer has reacted at least at one side of the molecule. Beyond this point only pendant reactive groups can react, so in this respect the situation resembles that of the step reactions again.

One difference remains, however. In the polacrylate studied here, one of the reactants, the radical, maintains a relatively high mobility through hydrogen transfer[15]. Although this process appears to be spatially limited such that the radicals themselves have a very long lifetime of several months at room temperature and under vacuum[12], they will still be able to convert pendant double bonds in their immediate vicinity. Results shown in *Table 3* and *Figure 5* indicate that reaction continues to proceed until the sample is deeply in the glassy state.

Effect of sample heating on T_g

The high values found for $T_{\tan\delta,\max}$ might cast suspicion on the method used. Indeed, the determination of a $T_{\tan\delta,\max}$ of 93°C implies that the sample has been heated to above that temperature. In addition to volume relaxation this may also cause additional, thermally activated curing. With the aid of *FT*i.r. analysis it can be checked whether or not the extent of double-bond conversion has increased upon a thermal scan in the d.m.t.a. For that purpose, directly after polymerization and determination of the extent of conversion, samples were heated in air up to 90°C at $4\,\mathrm{K\,min^{-1}}$. Then they were quenched and analysed again using *FT*i.r. Results in *Table 4* suggest the occurrence of a thermally induced reaction.

However, at the same time a substantial weight loss was observed. Assuming this weight loss to be due to evaporation of unreacted monomer, we calculated a corrected value which reflects the influence of heating only. Within experimental accuracy these figures match perfectly with the initial values, so we may conclude that the extent of double-bond conversion does not increase upon heating to 90°C. Nevertheless evaporation of monomer did occur and this will also affect the determination of $T_{\tan\delta,\max}$. However, in practice this effect may be of little importance since the weight losses of i.r. samples were observed with $7\,\mu\mathrm{m}$ thick coatings, while d.m.t.a. measurements were made using 0.5 mm thick samples. With the much thicker d.m.t.a. samples the relative weight loss is expected to proceed much more slowly than with the thin i.r. samples. This hypothesis was checked by recording the weight loss of one of these thicker samples during a thermal scan in air at a heating rate of $5\,\mathrm{K\,min^{-1}}$. The resulting t.g.a. curve is displayed in *Figure 6*; up to 90°C less than 1% of monomer has evaporated. Hence, the unusually high values of $T_{\tan\delta,\max}$ are caused neither by additional reaction nor by evaporation.

Table 4 Effect of heating on extent of double-bond conversion of HDDA, measured with *FT*i.r., and on weight of samples polymerized at different light intensities; approximately $7\,\mu\mathrm{m}$ thick coatings on silicon wafers, heated to 90°C at $4\,\mathrm{K\,min^{-1}}$ (cf. *Table 1*)

Light intensity ($\mathrm{mW\,cm^{-2}}$)	Exposure time (min)	x(*FT*i.r.) initial (%)	x(*FT*i.r.) 90°C (%)	Weight loss (%)	x(*FT*i.r.) 90°C, corr (%)
0.002	25	61.5	73	15	62
0.02	15	68	76	10	68.5
0.2	12	75	78.5	6	74
2	7.5	79.5	82.5	2	81

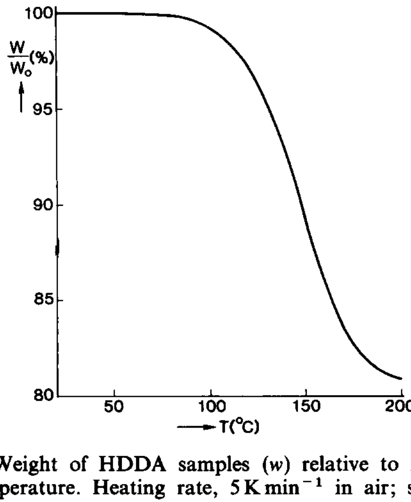

Figure 6 Weight of HDDA samples (w) relative to initial weight w_0 vs. temperature. Heating rate, $5\,\mathrm{K\,min^{-1}}$ in air; sample thickness, 0.5 mm; initiator; 0.25 wt% DMPA; exposure time, 25 min at $0.002\,\mathrm{mW\,cm^{-2}}$ and 20°C

Frequency dependence of T_g values of densely crosslinked networks

A final point to comment on is the determination of T_g of a densely crosslinked polymer. For reasons of sensitivity we have chosen to use d.m.t.a. D.s.c. usually gives somewhat lower values, but in the case of amine-cured epoxides the difference between d.s.c. and d.m.t.a. at a frequency of a few hertz was less than 10 K[6]. Likewise, for a series of eight different polyepoxide/amine networks Lee and Hartmann[25] reported an average difference of 9 K between d.s.c. and torsional pendulum measurements. According to Lee and Rutherford[26], d.m.t.a. at 1 Hz usually gives results very similar to dilatometric results obtained at $3\,\mathrm{K\,h^{-1}}$.

Several methods exist for extrapolation of T_g values to lower frequencies or scanning rates, but the frequency dependence of T_g has been found to be sensitive to the structure of the polymer[27]. Since it seems rather unlikely that correction of the T_g value of 93°C of HDDA photopolymerized at 20°C would reduce the 'gap' between T_g and T_{cure} to the commonly observed value of 25–35 K, we have refrained from a frequency correction.

CONCLUSIONS

In conclusion it can be stated that the photopolymerization of the diacrylate investigated does not stop upon vitrification but will continue in the glassy state at a decelerating rate. The same applies to the photoinitiation process.

In comparison with step reactions, the present chain polymerization yields a polymer with twice as large a difference between glass transition temperature and curing temperature.

It is proposed that β-relaxations may assist in sustaining the reaction in the glassy state.

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